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Use of Fillers, Pigments and Additives in Fouling-Release Coatings: a Literature Review

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Abstract

Polydimethylsiloxane (PDMS)-based fouling-release coatings represent a non-toxic alternative in the area of marine protection. Many researches and testing procedures are dedicated to the challenge of exploring of effective, reliable and high-performance constituents of the coatings – fillers, pigments and additives – in order to achieve the desired and long-lasting fouling-release properties.

Primarily, coating formulations are prepared on the basis of PDMS with inorganic fillers such as fumed silica (SiO_2), calcium carbonate (CaCO_3), pigments – titanium dioxide (TiO_2), iron oxide (Fe_2O_3) or carbon black (C), and other additives (e.g., silicone oils) [1, 2].

Silica and calcium carbonate can be used as agents to improve mechanical strength of the elastomeric material and provide superior thixotropic behavior to the coating formulations. Despite the fact that currently silica is more widespread in coating applications, calcium carbonate can also be competitive due to observed reduction of the surface modulus as a consequence of the dissolution under exposure to water [3]. Moreover, in many cases, calcium carbonate is added as extending filler in order to diminish expenses for silicone elastomers. As an additional option, pretreatment operations for silica can be considered as they ensure necessary hydrophilic/phobic properties alongside with easy dispersion in the PDMS matrix and lower moisture content. However, in this case, impaired reinforcement is observed [2].

One of the challenges in this field is to determine the right filler loading value. In case of a high filler content, the crucial fouling-release characteristics tend to deteriorate due to lower intrinsic hydrophobicity of the PDMS matrix, despite the fact that the tensile strength and toughness are on the suitable level [1]. This result is obtained without dependence on type of the filler [3]. It also should be mentioned, that several recent researches opened promising perspectives of embedding of natural sepiolite nanofibers ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$), single- or multi-walled carbon nanotubes (CWNTs and MWCNTs), modified graphite and graphene as fillers to maintain durability alongside with simultaneous fouling-release performance [1]. The explanation lies in the fact that addition of MWCNTs in low amounts helps to improve the properties mentioned above because of energetically favorable CH- π interactions between methyl groups of the PDMS and aromatic rings of the MWCNTs [5]. One of the major advantages of utilization of nano-structured fillers is that the particles are capable of providing significant interface area (by means of modifying the topography of the base) for interactions with the polymer matrix. This phenomenon gives an opportunity of potential enhancement of the mechanical strength without negative influence on the fouling-release properties. Another benefit of the nanoparticles is in altering of wetting abilities with forming self-cleaning or superhydrophobic surfaces [5]. Effect of the filler presence was tested by pseudobarnacles adhesion in order to estimate the tensile strength and fouling-release characteristics. It was discovered that the higher content of filler was, the greater pseudobarnacles adhesion strength and the lower fouling-release performance [1–3, 6].

As it is well known, besides giving color and opacity, pigments also influence mechanical (tensile strength, abrasion resistance, elastic modulus, tear energy) and adhesion properties in condensation-cured PDMS-based coatings [2]. In addition to this, pigments can enhance biofouling resistance. For instance, titanium dioxide possesses a capability of switching from hydrophobic to hydrophilic under UV-light exposure. The photocatalytic effect of TiO_2 gives an advantage in keeping the coating

surface clean via weakening of the adhesion forces between fouling species and the surface of the coating [7]. As a drawback, using pigments in some cases demands higher PDMS loading due to hindrance of the self-stratification effect of bringing the PDMS to the coating surface [6]. Normally, in order to estimate the influence of pigments, pull-off test is conducted revealing the adhesion strength of the coating on the underlying tie-coat [2].

According to the conducted experiments, it was concluded that silicone oils used as additives provide outstanding fouling-release properties due to appropriate critical surface tension and molecular mobility alongside with interfacial slippage and friction [3]. The principle of action of this additive type is in gradual migration of the molecules to the interface and leaching phenomenon which leads to the detachment of marine organisms and plants by slipping [4]. In other words, the fouling species settle onto the oils instead of the coating surface with a consequent release of the additive into the seawater. Usually, the amount of the additive in a coating formulation is relatively small (1-10 wt. %) as exceeding the limit of the additive content shortens service time span, causing surface damage and increasing coating susceptibility to biofouling [2]. Besides aforementioned silicone oils, several other types of the additives such as carboxyl-functionalized organosilicon polymers, low-molecular weight polyisobutylene, liquid paraffin-petrolatum, perfluorinated polymers or oligomers can be used to improve fouling-release properties [2]. In order to assess the efficiency of additives, immersion tests are typically conducted. During the tests, plates covered with coatings are put into seawater and cleaned after the specified period of time evaluating biofouling detachment characteristics [1, 2, 5, 8, 9]. Contact angle measurements are generally done by using the sessile drop technique giving a picture of the surface properties (hydrophobicity/hydrophilicity) of coatings [5, 7, 8].

Summarizing the information stated above, it should be noted that for the current coating formulations a lot of experiments and tests are required with the purpose of establishing the most effective and optimal ratio between the components. Further research must be done in the area of silica action alongside with the nano-structured compounds as a future replacement of traditional fillers. Likewise, the negative impact of a high filler loading on the fouling-release performance, must be thoroughly examined.

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